

Cite this: *J. Environ. Monit.*, 2012, **14**, 1814

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PAPER

**Determination of contaminant levels and remediation efficacy in groundwater at a former *in situ* recovery uranium mine†‡**Thomas Borch,<sup>\*a</sup> Nicholas Roche<sup>b</sup> and Thomas E. Johnson<sup>\*b</sup>

Received 28th January 2012, Accepted 10th May 2012

DOI: 10.1039/c2em30077j

There has been increasing interest in uranium mining in the United States *via in situ* recovery techniques. One of the main environmental concerns with *in situ* uranium mining is the potential for spreading groundwater contamination. There is a dearth of detailed analysis and information regarding the outcome of *in situ* uranium mine remediation to ascertain the environmental impacts. Regulatory measurements performed at a Wyoming *in situ* uranium mine were collected and analysed to ascertain the efficacy of remediation and potential long term environmental impact. Based on the measurements, groundwater sweeping followed by reverse osmosis (RO) treatment proved to be a highly efficient method of remediation. However, injection of a reductant in the form of H<sub>2</sub>S after groundwater sweeping and RO did not further reduce the aqueous concentration of U, Mn, or Fe. Low concentrations of target species at monitoring wells outside the mined area appear to indicate that in the long term, natural attenuation is likely to play a major role at reductively immobilizing residual (after remediation) concentrations of U(VI) thus preventing it from moving outside the mined area. Our analysis indicates the need for additional monitoring wells and sampling in conjunction with long term monitoring to better understand the impacts of the different remediation techniques.

**Introduction****Background**

Uranium is used to produce approximately 20% of all electricity consumed in the United States.<sup>1</sup> Domestic mining of uranium is based primarily on utilizing the most economic methods to extract the primarily low grade ore (<0.1%) that is common in the US.<sup>1,2</sup> The bulk of US uranium reserves available for economic extraction at \$50 per pound (275 million tons) is *via In Situ Recovery*

(ISR) (145 million tons), making ISR the most economical method for the majority of uranium deposits in the US.<sup>1</sup> Currently, there are six operational ISR mines (2010), with an additional six either partially licensed or licensed, and another four in standby or development.<sup>1</sup> There are no other currently active uranium mines in the US. Complete remediation has been accomplished at only a few facilities, although restoration of specific mine units of the various operational mines is ongoing.<sup>3</sup>

Several former ISR mine sites have been remediated, and significant amounts of data on ISRs collected for regulatory purposes, but to date, no complete scientific evaluation of the data, restoration process or the efficacy of the restoration process has been performed.<sup>4–8</sup>

**ISR process**

Uranium in the environment is found as two major species of differing oxidation states: U(VI), which is soluble and mobile, and

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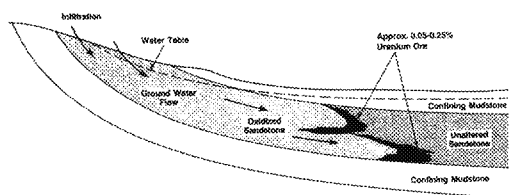
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† Published as part of a special issue dedicated to Emerging Investigators.

‡ Electronic supplementary information (ESI) available: A detailed map of mine unit A layout. See DOI: 10.1039/c2em30077j

**Environmental impact**

This project evaluated the remediation efficacy at a former *in situ* recovery uranium mine based on a statistical analysis of data publicly available to help determine the potential long term environmental impact. A combination of groundwater sweeping and reverse osmosis proved to be an efficient remediation approach. The relatively low concentrations of key species such as U observed at monitoring wells outside the mined area indicate that natural attenuation likely plays an important role in controlling the mobility of redox sensitive contaminants.



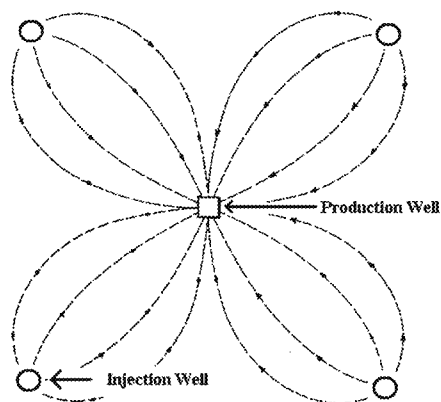
**Fig. 1** Creation of uranium roll front by precipitation (adapted from U.S. Nuclear Regulatory Commission 2007).<sup>6</sup>

$U(IV)$ , which is sparingly soluble and usually precipitates as  $UO_2(s)$  (uraninite).<sup>9</sup> In areas with naturally high uranium concentrations, dissolved oxygen in groundwater will oxidize uranium to its  $U(VI)$  species. As the groundwater continues down a hydrological gradient into a reducing environment, the oxygen content becomes depleted and the uranium will become reduced to its  $U(IV)$  species and precipitates.<sup>6</sup> The precipitation process eventually creates a roll front of uranium bearing sands, as seen in Fig. 1.

If a potential site is deemed geologically feasible for ISR uranium mining, then the uranium is recovered from the roll front through the use of wells. ISR is geologically feasible when a permeable ore body is within a confined aquifer, and located such that groundwater away from the ore body cannot be contaminated. Wells are typically drilled in square patterns, with a production well in the middle of the square (see Fig. 2).

Oxygen ( $O_2$ ), or other oxidizing agents such as  $H_2O_2$ , and a carbon alkaline (generally  $CO_2$ ) are added to the water that is pumped into the injection wells (Fig. 3), and the water then flows towards the production well due to the positive net flux of water being pumped out. The oxygen in the water oxidizes the  $U(IV)$  into its soluble  $U(VI)$  form.<sup>11</sup> The addition of  $CO_2$  buffers the pH of the water and promotes the formation of highly stable uranyl {or  $U(VI)$ } (hydroxy)carbonate ions, further enhancing the  $U(VI)$  solubility. The uranium bearing water is then pumped back to the surface, where the uranium is extracted through an ion exchange process. The water is then reoxygenated before being pumped back into the injection wells.

The main environmental concern from ISR mining is the transport of contaminated water into a regional aquifer, whose water may be consumed by livestock or humans. Another concern is the possible diffusion or leaching of contaminants



**Fig. 2** Typical well pattern (with permission from PRI, 2000).<sup>10</sup> The four wells which make up the points on the square are the injection wells and the inner well is the production well.

through the soil and subsequent uptake by plants, which can then enter the human food chain by consumption of either the plants or animals which have eaten the plants. The third risk of ISR mining is the potential for a spill or accident (e.g. release of contaminated water).<sup>6</sup>

### Post-mining: remediation

Mining companies, as part of their license contract, must remediate the mine site back to preexisting conditions, or as close as reasonably possible based on regulatory guidance. This entails ensuring that the groundwater contaminant concentration levels reach agreed upon standards. There are several methods used by the mining companies in order to remediate the groundwater. These methods include groundwater sweep, reverse osmosis, chemical reductant, bioremediation, and natural attenuation.

Groundwater sweep remediation is accomplished by continually pumping water from the production well, with no water pumped into injection wells. The groundwater which is pumped up through the production well is then disposed of through various methods.<sup>12</sup> Regional groundwater then restores the aquifer through the hydrological gradient created by pumping the high concentration water from the production well and the regional water replacing it. Reverse osmosis remediation is where contaminated water is pumped to the surface treated through reverse osmosis then re-injected into the aquifer. Injecting a chemical reductant, such as  $H_2S$ , to restrain further oxidation reactions within the roll front and cause contaminants to precipitate back onto their surrounding environment is another method of remediation.<sup>12</sup> Bioremediation consists of using naturally occurring bacterial species such as *Geobacter* to reduce contaminants to their insoluble form through natural metabolic pathways. Electron donors such as ethanol are injected into the wells, increasing proliferation of naturally occurring bacteria, and resulting in re-precipitation of contaminants.<sup>13,14</sup> For example, bacteria reduce  $Fe(III)$  to  $Fe(II)$  which can reduce  $U(VI)$  (soluble) to  $U(IV)$  (insoluble) and bacteria can also directly reduce  $U(VI)$  to  $U(IV)$ , resulting in  $U(IV)$  precipitation.<sup>15,16</sup> There are three main natural attenuation processes: adsorption, dispersion, and precipitation. Adsorption occurs when a solid material comes into contact with the groundwater. The solid material will attract the ions in the groundwater, and the ions will adsorb onto the surrounding material. Dispersion occurs when a fluid flows through a porous medium. It arises due to the different flow paths and flow velocities established by the pore diameters and the pore configurations in the host rock. The contaminants in the groundwater will disperse and mix with the uncontaminated groundwater, thus diluting the concentrations over a period of time. Precipitation is caused by the reduction of sulfate to sulfide due to reducing conditions that were not disturbed by mining. As the groundwater reverts to its original flow direction, towards the reduced side of the roll front, certain minerals, such as pyrite and uraninite, will precipitate out of the groundwater into the surroundings as they encounter the reducing environment.<sup>17</sup>

### Post-mining: determination of remediation efficacy and goals

There is limited information available on how best to monitor efficiency and efficacy, and how long to monitor *in situ* uranium

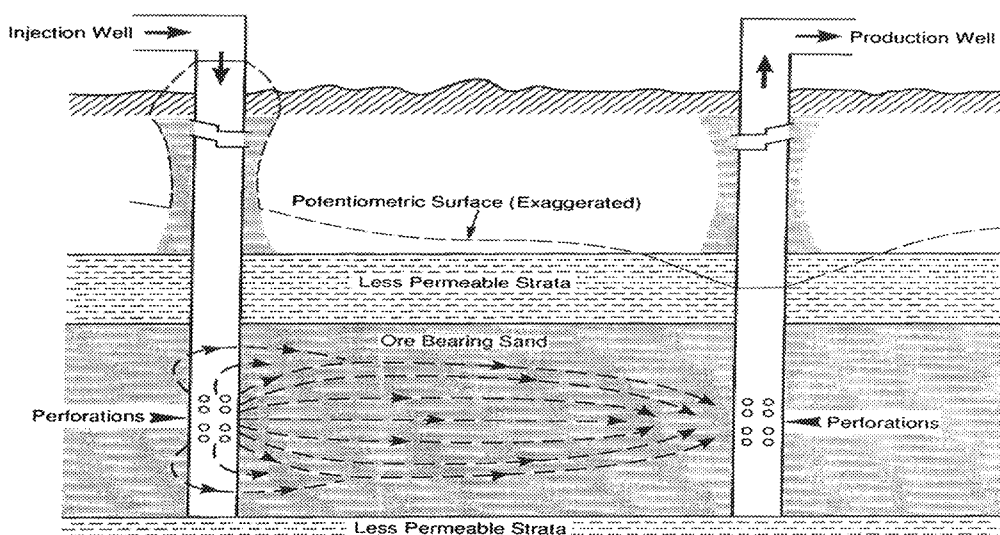


Fig. 3 Process of ISR uranium mining (adapted from U.S. Nuclear Regulatory Commission 2007).<sup>6</sup>

mines during and post-remediation. Furthermore, the specific fate of the remediated species has not been well documented.<sup>18</sup>

Thus, the objectives of this paper are to (1) evaluate the efficacy of groundwater sweep remediation in combination with reverse osmosis (RO) and H<sub>2</sub>S (chemical reductant) treatment and (2) determine the time needed for site stabilization and immobilization of target contaminants.

## Methods

### Site general information

The Smith Ranch Highland Uranium Project (HUP) is an *in situ* uranium mine site currently operated by Cameco Corporation (previously operated by Power Resources, Inc.), located in central Converse County, Wyoming, in the southern portion of the Powder River Basin. Cameco Corporation has several mine units currently in operation at the HUP. The mine unit of interest in this study is mine unit A, or the A-Wellfield (see detailed map in ESI†).

### Mine specifications

The Highland Sand Group, containing uranium roll fronts, are a part of the lower Wasatch Formation of early Tertiary age, and regionally forms a single aquifer and consists of fluvial sandstones of the Fort Union Formation. The Wasatch Formation is nearly flat in this vicinity, with a regional dip of <0.5 degrees to the east and north. Mine unit A “was installed in a lens of sand surrounding an isolated uranium roll-front which had infiltrated downwards from the sand.”<sup>19</sup> The sand was discontinuous; however the western boundary was well defined (near well M-8). There is shale separating the two sand aquifers, with a less than 0.6 m (2 feet) thick elongated northeast to southwest trending zone and the two aquifers are interconnected. Monitoring during and after mining was conducted such that the trending zone was partially enclosing the aquatard (see ESI† for a detailed map). The average depth of mine unit A, 161.5 m (530 feet), is deeper than the typical aquifers used for domestic and livestock supply in the surrounding area. The gradient in the regional groundwater is approximately 0.6 degrees in the north-westerly

direction,<sup>19</sup> and the average natural flow rate of the groundwater is estimated to be 1.7 m (5.6 feet) per year generally eastward, with local southerly or northerly components.<sup>10</sup> Groundwater flow was established prior to mining activities based on groundwater recharge and discharge areas and analysis of water level data. When in operation, the A-Wellfield was composed of 31 production patterns divided into three sections: A-1, A-2, and A-3. The A-Wellfield also had 14 monitoring wells in a ring surrounding the wellfield. The monitoring ring and monitoring wells above and below the aquifer were used to detect excursions.

### Source of data

Data were obtained from publicly available Nuclear Regulatory Commission (NRC) and Wyoming Department of Environmental Quality (WYDEQ) reports concerning Cameco’s Smith Ranch Highland Uranium Project. Uranium was mined in the A-Wellfield from January 1988 until July 1991.<sup>10</sup> Restoration of groundwater in the A-Wellfield was conducted from July 1991 to October 1998, using the groundwater sweep, reverse osmosis, and chemical reductant remediation methods. The groundwater sweep was utilized from July 1991 until June 1994 (utilizing 13 million gallons), followed by the reverse osmosis method from June 1994 until November 1997. Hydrogen sulphide (H<sub>2</sub>S) gas was selected as the reductant to be used for phase 3 of groundwater restoration, and this method was started in May 1998 and continued until October 1998. The stabilization period was from February 1999 until October 1999, and the successful restoration of mine unit A was satisfactorily demonstrated to the Wyoming Department of Environmental Quality (WYDEQ). The mine unit has been inactive since declared remediated in 1999. Monitoring is still being conducted at selected wells as part of the long term monitoring plan.

The study locations were selected based on the detailed information available for wells MP-4, I-21, LTM-4, M-3, and M-4. Since this study was not sponsored, funded or authorized by Cameco (current mine operators and owners of the data), only publicly available information submitted as a part of the regulatory process was available. During restoration, regulatory reporting of detailed well by well chemistry is not required, and,

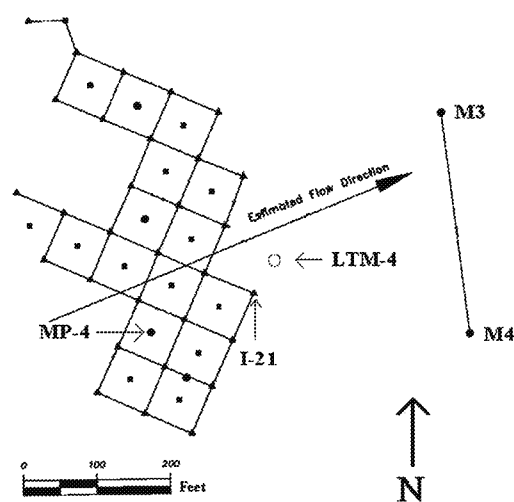
for regulatory purposes, is unnecessary. Some well by well detail is available for the six month period following the declaration of completion of restoration, in order to establish wellfield “stability” per WYDEQ regulation. The dataset used for analysis is unique, as the WYDEQ identified these wells as being those with the highest concentrations of constituents, and of most interest to follow long term post-restoration completion. Detailed chemistry for the entire mine unit may exist, but, if so, it is proprietary to Cameco since it is not necessary to make regulatory decisions, and not readily available for scientific analysis.

### Remediation efficacy parameters chosen for mine unit A

Concentration levels from 2005 to 2010 were only available for six parameters: naturally occurring uranium (U-nat), radium-226 (Ra-226), chlorine (Cl), alkalinity (Alk), pH, and manganese (Mn). Data on these six variables were obtained from five wells in the A-Wellfield: I-21, MP-4, LTM-4, M-3, and M-4 (see Fig. 4). Well I-21, which was previously an injection well, and well MP-4, which was previously a (monitored) production well, are located within the grid of injection and production wells. Wells M-3 and M-4 are monitoring wells located roughly 300 feet from the A-Wellfield. Well LTM-4, which is between the grid and the monitoring wells, was drilled as part of the long term monitoring project, and is roughly 50 feet to the east of well I-21, in the flare from the production zone. These wells were chosen by Cameco Corporation and the WYDEQ for the long term monitoring of contaminants over time as groundwater flowed. Well MP-4 had the highest concentration of three elements of concern (U, Ra and Se) and MP-4 along with the associated downstream wells were selected for long term monitoring by Cameco and WYDEQ.

### Statistical analysis of long term monitoring data

Statistical analysis was performed using Statistical Analysis Software (SAS V. 9.0, Cary, NC). First, the data were tested for



**Fig. 4** Well locations of MP-4, I-21, LTM-4, M-3, and M-4 in the A-Wellfield. MP-4 indicates monitored production well 4, I-21 indicates injection well 21, LTM-4 indicates long term monitoring well 4, M-3 and M-4 indicate monitoring wells 3 and 4. See ESI† for a detailed map (adapted from PRI, 2000).<sup>10</sup>

significant changes in concentrations of each parameter in each well using regressions of the natural logarithm of concentration on elapsed days since January 1<sup>st</sup>, 2005. The null hypothesis of no change in the slope of the regression line was tested using the *T*-test at the 99% confidence level.

The second method used analysis of covariance (ANCOVA) to test for significant differences in the regression slopes among wells for a particular parameter. The ANCOVA analyses of differences in slopes among wells were performed separately for the two monitoring wells (M-3 and M-4) and the three wells in or near the field (I-21, MP-4, and LTM-4). The null hypothesis of equal slopes among wells for a parameter was tested using the SAS function proc glm. Significance was determined at the 95% confidence level, using the Type III sum of squares error method for the interaction between wells and days. If a significant interaction term occurred, indicating that variables could be dependent upon each other, the slopes for the various wells were compared using linear contrasts to determine which wells differed.

The third method tested for differences in means between the wells, and utilized the permutation analysis from SAS. Similar to the Monte Carlo method, the permutation analysis randomly reassigned the 50 data points to five bins, representing the five wells. SAS then analyzed the differences between specified combinations of means. These combinations included the following: the mean of the production zone wells (I-21 and MP-4) was compared to well LTM-4; the mean of the production zone wells was compared to the mean of the monitoring wells (M-3 and M-4); and well LTM-4 was compared to the mean of the monitoring wells. The comparisons were repeated 20 000 times to produce statistically significant values, and a distribution of differences between means was produced. The actual difference between specified means was then compared to the distribution to determine if the difference between means is improbably larger or smaller than that which would be expected. Thus, the null hypothesis that the pattern in the data was no different from that which would be expected if the observations were assigned randomly to the different bins was tested against the constructed distribution. If a result was determined to be significant, then a large positive difference in means or a large negative difference in means existed. As the analysis was two-tailed, an improbability level, which is analogous to a significance level, of  $p < 0.005$  was used.

## Results

### Groundwater quality

The groundwater quality pre-mining was designated as Wyoming Class of Use 5 (commercial-mineral) due to the elevated concentrations of dissolved radium. The water was found to be unsuitable for domestic, irrigation, or livestock purposes. The concentrations of contaminants were generally elevated at the end of restoration, with uranium, arsenic, iron, manganese, and selenium having levels increased by at least a factor of five from their baseline concentration levels.<sup>10</sup> The concentration levels at the various stages of mining are shown in Table 1. Data in Table 1 also indicate that the use of H<sub>2</sub>S after groundwater sweeping and RO did not further improve the water quality.

Although the concentration levels post-restoration were higher than baseline concentration, the water "Class of Use" standards established by the WYDEQ deemed to have been met. Also, 30 of 35 parameters had concentrations post-restoration below limits for any Class of Use (see Table 2).

### Covariance analysis

Covariance analysis was performed to ascertain differences in concentration over time. The covariance analysis results yielded statistically significant differences in slopes among the inside wells (I-21, MP-4, and LTM-4) for natural uranium, chlorine, and manganese. For natural uranium, I-21 was decreasing, MP-4

was increasing, possibly indicating oxidation of U, and LTM-4 was showing no change over time. For chlorine, wells I-21 and LTM-4 were decreasing while well MP-4 was showing no change over time. For manganese, well LTM-4 was increasing (possibly indicating a reducing environment) while wells I-21 and MP-4 were showing no change over time. There was no consistent pattern as to which wells would be increasing or decreasing for a given parameter.

### Regression analysis

Statistically significant ( $p < 0.01$ ) regression slopes were observed for natural uranium, chlorine, and manganese (see Table 3). No

**Table 1** Average water quality at wells MP-1 through MP-5 in the A-Wellfield for various stages of operations ( $n = 5$ ).<sup>10</sup> All values in mg L<sup>-1</sup>, except for pH in standard units and Ra in pCi L<sup>-1</sup>. The pH value was measured in the laboratory and was affected by the unavoidable degassing of the water during sampling. The actual values in the aquifer are believed to have been closer to pH 6.0. The range of values is in parenthesis. Complete information on values for other wells is not available. See ESI† for a detailed map of mine unit A and well locations

	Baseline Aug. 1987	Post-mining July 1991	Pre-H <sub>2</sub> S May 1998	Post-restoration Feb. 1999	% of baseline post-restoration	EPA primary standards for drinking water
Ca	44.1 (43.8–44.4)	313.4 (296.0–343.0)	68.6 (35.2–117.0)	73.4 (64–83.0)	166	—
Mg	9 (8.6–10.2)	59.5 (53.5–63.6)	12.4 (6.1–21.6)	13.5 (7.8–16.2)	150	—
Na	55 (52.5–55.6)	80.8 (77.9–83.8)	37.4 (32.4–51.6)	42.2 (35.1–57.0)	77	—
K	8 (6.1–12.1)	13.4 (13.1–14.1)	4.7 (3.0–6.8)	4.4 (3.3–5.9)	55	—
CO <sub>3</sub>	0	0	0	0	—	—
HCO <sub>3</sub>	215 (207.0–223.0)	720.2 (690.0–810.0)	242.21 (122.0–401.0)	256.6 (211.0–314.0)	119	—
SO <sub>4</sub>	91 (89.4–94.5)	380.6 (364.0–413.0)	83.9 (61.6–108.0)	127.2 (94.0–159.0)	140	250
Cl	4.7 (4.2–5.1)	212.6 (188.0–239.0)	14.4 (4.0–34.9)	18 (15.0–20.0)	383	250
NH <sub>4</sub>	0.1 (0.11–0.15)	0.7 (0.08–1.97)	0.2 (0.06–0.46)	0.29 (0.12–0.54)	290	0.5
NO <sub>2</sub>	0	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	—	1
NO <sub>3</sub>	0	0.2 (0.10–0.41)	0.1 (0.10–0.10)	0.1 (0.10–0.10)	—	10
F	0.2 (0.10–0.17)	0.2 (0.13–0.29)	0.14 (0.11–0.20)	0.15 (0.11–0.18)	75	4
SiO <sub>2</sub>	16 (15.40–16.50)	20.5 (17.40–22.10)	12.6 (9.50–16.50)	11.9 (7.20–15.70)	74	—
TDS	330 (312–352)	1507 (1420–1593)	342 (227–532)	410 (366–443)	124	500
Cond.	525 (506–562)	2390 (2346–2468)	579 (396–901)	647 (582–697)	123	—
Alk.	177 (170–183)	591 (566–664)	199 (100–329)	211 (173–258)	119	—
pH	8 (7.65–8.28)	6.78 (6.54–7.20)	7.25 (6.71–7.73)	7.31 (7.09–7.53)	91	6.5–8.5
Al	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	100	—
As	0.001 (0.001–0.002)	0.001 (0.001–0.002)	0.01 (0.001–0.049)	0.03 (0.001–0.092)	3000	0.05
Ba	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	100	2
B	0.1 (0.1–0.1)	0.1 (0.1–0.14)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	100	0.75
Cd	0.01 (0.01–0.01)	0.03 (0.01–0.1)	0.005 (0.005–0.005)	0.005 (0.005–0.005)	5	0.005
Cr	0.05 (0.05–0.05)	0.05 (0.05–0.05)	0.05 (0.05–0.05)	0.05 (0.05–0.05)	100	0.1
Cu	0.01 (0.01–0.02)	0.02 (0.01–0.04)	0.03 (0.01–0.10)	0.01 (0.01–0.01)	100	1
Fe	0.05 (0.05–0.05)	0.05 (0.05–0.05)	1.32 (0.05–3.55)	1.3 (0.44–2.20)	2600	0.3
Pb	0.05 (0.05–0.05)	0.05 (0.05–0.05)	0.05 (0.05–0.05)	0.05 (0.05–0.05)	100	0.015
Mn	0.03 (0.01–0.03)	0.66 (0.07–1.08)	0.41 (0.14–0.54)	0.49 (0.30–0.80)	1633	0.05
Hg	0.001 (0.001–0.001)	0.001 (0.001–0.001)	0.001 (0.001–0.001)	0.001 (0.001–0.001)	100	0.002
Mo	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	100	—
Ni	0.05 (0.05–0.05)	0.08 (0.05–0.14)	0.05 (0.05–0.05)	0.05 (0.05–0.05)	100	—
Se	0.001 (0.001–0.004)	0.99 (0.313–1.590)	0.16 (0.001–0.504)	0.07 (0.001–0.343)	7000	0.05
V	0.1 (0.1–0.1)	0.19 (0.1–0.29)	0.1 (0.1–0.1)	0.1 (0.1–0.1)	100	—
Zn	0.01 (0.01–0.02)	0.04 (0.01–0.12)	0.01 (0.01–0.01)	0.01 (0.01–0.01)	100	5
U	0.05 (0.02–0.07)	40.19 (24.40–62.50)	3 (0.08–9.86)	3.53 (0.17–8.35)	7060	0.03
Ra	675 (67–916)	3286 (1974–5984)	1056 (284–3030)	1153 (293–3220)	171	5

**Table 2** Average water quality post-restoration for wells MP-1 through MP-5 (see Table 1 for details). *Note:* in general, Wyoming classifications of water quality are as follows: Class 1 – outstanding quality water, Class 2 – fisheries and drinking water, Class 3 – aquatic life other than fish, and Class 4 – agriculture, industry, recreation and wildlife

At or below baseline	Above baseline, but below limits for any Class of Use	Above baseline and above limits for Classes 1–3
Na, K, CO <sub>3</sub> , NO <sub>2</sub> , NO <sub>3</sub> , F, SiO <sub>2</sub> , Al, Ba, B, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Zn, V	NH <sub>4</sub> , Ca, Mg, HCO <sub>3</sub> , Cl, TDS, conductivity, Alk., pH, SO <sub>4</sub> , As	U, Fe, Mn, Se, Ra

**Table 3** Analysis of regression lines. The six instances of significant regression slopes. Significance level at 99%. Note that negative slope indicates that the parameter has decreased in concentration over the five years post-remediation. Positive slope indicates that the parameter has increased in concentration over the five years post-remediation. All other parameters did not change, based on the value of  $p = 0.05$

Parameter	Well (type)	Slope (% per year)
Natural uranium	I-21 (injection)	−30.0
Natural uranium	MP-4 (production)	4.4
Chlorine	I-21 (injection)	−3.0
Chlorine	LTM-4 (long-term monitoring)	−5.0
Manganese	LTM-4 (long-term monitoring)	7.5
Manganese	M-4 (monitoring)	−7.2

significant trends of either increasing or decreasing values with time were observed for radium, alkalinity, or pH. No statistically significant trends of increasing values with time were observed for either of the two monitoring wells. Slopes were expressed as percent change per year, and most slopes indicated rates of change per year of less than 10% except for natural uranium in injection well I-21, where concentrations were declining at a rate of 30% per year. There were no significant differences in slopes between the monitoring wells except for the decrease in levels of manganese in well M-4.

#### Analysis of differences between means

The average mean of the inside wells (MP-4 and I-21) was significantly higher than the average mean of the monitoring wells for all parameters except pH. The mean of well LTM-4 either was equal to the average mean of the inside or monitoring wells or was less than the inside wells but greater than the monitoring wells (see Table 4).

The graphs of the two main parameters of interest, U-nat and Ra-226, are shown in Fig. 5 and 6. Due to the large difference in concentration levels among the wells, the ordinate is on a logarithmic scale. We were unfortunately not able to obtain data covering the immediate time period after remediation (*i.e.*, February 1999 to January 2005). However, Table 1 clearly shows that the post-restoration analysis of U and Ra in MP-1–5 conducted in 1999 resulted in concentrations very similar to the

concentrations observed at MP-4 nearly six years later (Fig. 5 and 6), indicating that the concentration of these species likely had already stabilized.

## Discussion

### Covariance and regression analysis

Statistical analysis was performed to ascertain which parameters had significant changes over time and then the importance of each.

### Parameter changes prior to 2005

Since the water between I-21 and LTM-4 is replaced in about nine years (based on a flow rate of 1.7 m per year and a distance of 15 meters), it is reasonable to assume that U has been removed primarily due to natural attenuation, since the H<sub>2</sub>S treatment did not result in any significant change in U concentration (Table 1). It should be mentioned that the high bicarbonate concentrations (avg. 4 mmol L<sup>−1</sup>) will promote the formation of U(VI)–carbonate complexes and likely prevent the reduction of U(VI) by H<sub>2</sub>S due to the lower redox potential of these U(VI) species.<sup>20,21</sup> The As concentration is approximately 3 times higher after the H<sub>2</sub>S treatment, indicating that not all As precipitated as sulfide bearing mineral phases, but As might also have been released due to reductive dissolution of Fe(III) oxides and secondary Fe mineral formation.<sup>22</sup> The H<sub>2</sub>S treatment also did not influence the aqueous Fe concentration indicating that sulphide-bearing Fe minerals such as pyrite did not form. There are at least three additional reasons for why H<sub>2</sub>S may have had little effect. First, the injection well (I-21) is located far enough away from the MP wells, that there was insufficient mixing, and reactions were limited. Secondly, it is possible that soluble Fe(II) was initially precipitated out as FeS<sub>x</sub>; however, the sample indicating the presence of aqueous Fe was collected several months after the H<sub>2</sub>S injection. Thus, it is likely that biologically induced reductive Fe dissolution allowed the Fe(II) to re-enter the water after the pool of sulfide had been exhausted. Thirdly, there are indications (Table 1) that averaging data to ascertain the efficacy of H<sub>2</sub>S injection is not an optimal technique. Baseline data for MP-4 might have been misleading, since overall averages were used to determine the efficacy, and MP-4 seemed to trend higher, possibly skewing results. Again, additional samples and more frequent sampling would provide a more clear understanding of the response of the environment to the addition of H<sub>2</sub>S and the apparent lack of impact.

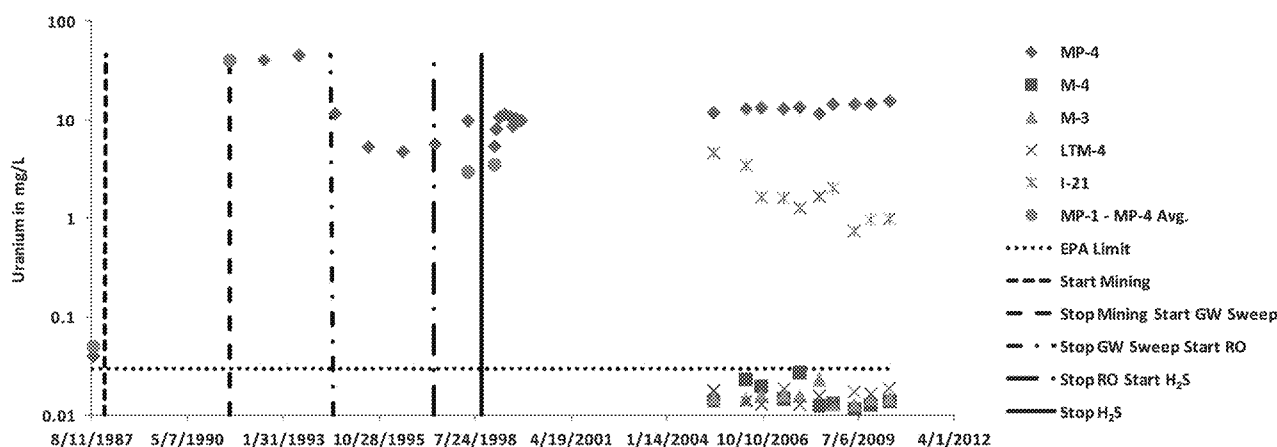
### Parameters with no significant changes from 2005–2010

The temporal behaviour of concentration levels among the wells is similar for the parameters of alkalinity, pH, and radium.

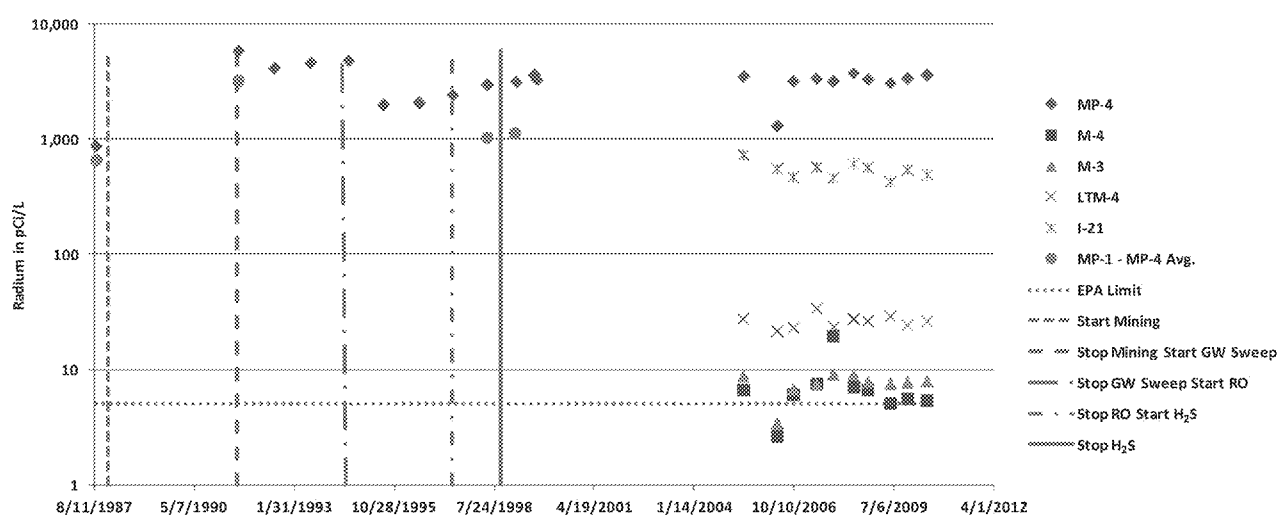
Radium can be immobilized by adsorption to Fe oxides or precipitation with sulphates or co-precipitation with Ba bearing minerals. There are also no significant changes in the slopes of the regression lines for these parameters. If the levels for the three parameters are consistent over time among wells due to the behaviour of the parameters, then it is reasonable that the levels should also remain constant at a particular well. These results would imply that the flux of these parameters is stable across all

**Table 4** Analysis of differences between means. Significance level at 0.005. Inside wells: wells in the mineralized region, I-21 and MP-4. Monitoring wells: M-3 and M-4

Parameter	Differences in means
Alkalinity (mg L <sup>−1</sup> )	Inside wells (394) > LTM-4 (327) > monitoring wells (185)
pH	Monitoring wells (7.7) = LTM-4 (7.7) > inside wells (7.1)
U-nat (mg L <sup>−1</sup> )	Inside wells (8.35) > LTM-4 (0.016) = monitoring wells (0.016)
Ra-226 (pCi L <sup>−1</sup> )	Inside wells (2096) > LTM-4 (27.0) > monitoring wells (7.6)
Chlorine (mg L <sup>−1</sup> )	Inside wells (18) = LTM-4 (20.8) > monitoring wells (3.4)
Manganese (mg L <sup>−1</sup> )	Inside wells (0.48) > LTM-4 (0.087) > monitoring wells (0.032)



**Fig. 5** Concentration ( $\text{mg L}^{-1}$ ; log scale) vs. time (y) of sampling for U-nat. MP-4 = monitored production well, I-21 = injection well, LTM-4 = long term monitoring well, M-3 and M-4 = monitoring wells ("outside mined area"). EPA limit = EPA primary standards for drinking water.



**Fig. 6** Concentration ( $\text{pCi L}^{-1}$ ; log scale) vs. time (y) of sampling for Ra-226. MP-4 = monitored production well, I-21 = injection well, LTM-4 = long term monitoring well, M-3 and M-4 = monitoring wells ("outside mined area"). EPA limit = EPA primary standards for drinking water.

five wells. The implication is that the restoration was successful for these parameters.

#### Parameters with significant changes from 2005–2010

There was a difference in the temporal behaviour of the concentration levels among the inside wells for the parameters of uranium, manganese, and chlorine. From the regression analysis for natural uranium, it can be seen that the slope of concentration levels over time at well I-21 declines, the slope of well MP-4 slightly increases, and the slope of well LTM-4 remains constant. This indicates that the levels are not in equilibrium, and could be due to changing conditions or a net flux of contaminants into the area.

Uranium is sensitive to reduction–oxidation (redox) conditions, and these conditions will vary depending on the location of the well. This could possibly explain the differences in the temporal behaviour among the wells for uranium as well I-21 was used as an injection site during the chemical reductant phase of

remediation. Therefore, the concentration levels of uranium could be decreasing due to that area still being in a predominantly reducing environment (as indicated by Table 3). Well MP-4 is situated in the middle of the production zone, and a slight oxidizing environment in that zone could still exist, leading to the increase over time. Another explanation is that the net flux for the uranium concentration is positive for MP-4 and negative for I-21. The trend at I-21 could be due to more uranium being attenuated by natural processes or leaving with groundwater than the influx of uranium. It is very difficult to speculate or model the most likely natural attenuation processes controlling the fate and transport of U at this site due to the general lack of hydrological and biogeochemical data. In addition, numerous studies have discussed the many potential natural attenuation mechanisms but only few studies have attempted to model natural attenuation kinetics.<sup>23–25</sup> The higher Mn concentration inside the mined area indicates continued reducing conditions, even after restoration has been completed (Table 4). Additionally, the high Fe concentration indicates that reduction may still



be taking place. Because of these various alternate possible explanations and data from only three wells, there are insufficient data to determine the cause of the trends in the regression lines.

### Monitoring wells

There were no changes in the slopes of the regression lines, except the slight decrease (7.2% per year) in the slope of M-4 for manganese. There were also no significant temporal differences between wells M-3 and M-4 for any of the parameters, implying that the groundwater chemistry and redox environment are stable at that point on the monitoring ring, and have not been affected by the mining operations.

Stability at the monitoring ring indicates that there is a strong potential for natural attenuation, since the conditions were originally reduced or reducing (low redox potential) and redox measurements conducted post-restoration showed clear evidence for Fe reducing conditions (Table 5). The concentration levels are also similar to baseline levels at wells MP-1 through MP-5 (Table 6).

Interestingly, well LTM-4 is located approximately 16.1 m (53 feet) down gradient of the flare zone of well I-21 where uranium concentration levels are declining at a rate of 30% per year. The groundwater will have had time to migrate from the production zone into the area of well LTM-4 at the estimated migration rate of 1.7 m per year (5.6 ft per year) in the 10 years which have elapsed. Thus the water at LTM-4 has probably only been replaced one time since the end of remediation. However, no statistical changes occurred in the concentration levels of uranium for LTM-4, where the mean levels are statistically similar to those of M-3 and M-4; yet, the levels of manganese at well LTM-4 are increasing by 7.2% per year. Manganese generally exists in three oxidation states (+2, +3, and +4). Mn(II) is generally soluble, but precipitates out of solution as Mn(IV) (hydr)oxides when oxidized.<sup>16</sup> Uranium behaves opposite in that it is generally soluble in its oxygenated species of U(VI), but generally much less soluble when reduced to its U(IV) species. Since well I-21 was used as an injection well during the reductant phase of remediation (the last phase to be completed), it is possible that the reducing environment has migrated to well LTM-4, and the altered redox conditions are causing the decrease in uranium levels and the increase in manganese levels. Further, the Cl concentration at LTM-4 compared to M-3 and M-4 (Table 4) provides some evidence that water from the mine unit has indeed reached LTM-4, but other less soluble minerals are being naturally attenuated. It would be interesting to add

**Table 6** Comparison of baseline water quality values with monitoring wells

Parameter	Average baseline values for MP-1 through MP-5	Average values for M-3 and M-4 post-remediation	LTM-4 post-remediation
Cl (mg L <sup>-1</sup> )	4.7	3.4	20.8
ALK (mg L <sup>-1</sup> )	177	185	327
pH (mol L <sup>-1</sup> )	8.0	7.9	7.7
Mn (mg L <sup>-1</sup> )	0.030	0.032	0.087
U nat (mg L <sup>-1</sup> )	0.050	0.016	0.016
Ra-226 (pCi L <sup>-1</sup> )	675	7.6	27.0

future data from LTM-4 to affirm trends and provide information on natural attenuation.

### Conclusion

No long term studies of the fate of a restored *in situ* uranium mine could be located in the literature, and it is believed that this is the first documented attempt to examine long term conditions post-mining.

Based on the measurements, groundwater sweeping followed by reverse osmosis (RO) treatment proved to be a highly efficient method of remediation. Injection of a reductant in the form of H<sub>2</sub>S after groundwater sweeping and RO did not further reduce the aqueous concentration of U, Mn, or Fe. The efficacy of H<sub>2</sub>S injection and impact on constituent concentration require further study to ascertain why it was ineffective. However, the formation of U(VI)-carbonate complexes is the most likely reason for the lack of U(VI) reduction by H<sub>2</sub>S.<sup>21</sup>

The subsurface of Mine Unit A was strongly reduced before mining was initiated. It is likely that sulfate reducing conditions were initially present. However, pockets of O<sub>2</sub> may exist within the subsurface where H<sub>2</sub>S did not permeate and fully restore the redox potential to baseline conditions. The lack of permeation of a reductant may explain why certain wells still seem to be situated in an oxic or Fe(III) rich zone resulting in high or above baseline concentrations of U(VI).<sup>26</sup> Since Fe(III) is still present, adsorption sites are most likely still available for Ra, so long term concentration of Ra may decrease. Sulfate is also present at fairly high concentrations; thus sulfate reduction is likely to control the redox potential in zones with no O<sub>2</sub> or low Mn(IV), Fe(III), and NO<sub>3</sub> concentrations within the sub-surface environment. However, the fairly high concentration of sulfate (*i.e.*, avg. 127 mg L<sup>-1</sup>) did not seem to cause precipitation of the high Ra radioactivity during the observed period. In addition, since Fe

**Table 5** Wells analyzed for pH, temperature, dissolved oxygen, Eh, pe, Fe(II) and Fe total post-restoration. M7, M16, M10A, and M12 are A-Wellfield ring wells and MP3 and MP4 are A-Wellfield ore zone wells

Well	Date	Field pH	Field temp. (°C)	Field diss. O <sub>2</sub> (mg L <sup>-1</sup> )	Field Eh (mV)	Field pe	Field Fe(II) (mg L <sup>-1</sup> )	Field Fe-tot. (mg L <sup>-1</sup> )
M7	10/30/00	7.9	14.6	7	242	4.1	0.1	0.2
M16	10/30/00	7.8	14.1	1	121	2.0	1.0	2.0
M10A	12/01/00	7.6	14.2	2	221	3.7	0.3	0.4
M12	12/01/00	7.7	14.9	1	102	1.7	0.4	0.4
MP3	12/01/00	6.3	15.2	0	164	2.8	1.0	2.0
MP4	12/01/00	6.2	14.7	1	276	4.7	0.4	0.4



reducing conditions were confirmed at multiple wells shortly after the restoration had ended (Table 5) it is likely that Fe(III) is outcompeting sulfate as an electron acceptor.

U, Cd, Pb, and Ra were above EPA standards for drinking water before mining, while U, Fe, Mn, Se, and especially Ra were above baseline and EPA drinking water standards after remediation.

The very low concentrations of target species (U and Ra) at the two monitoring wells indicate that natural attenuation is likely to play a major role at immobilizing residual (after remediation) concentrations of U(VI) species, thus preventing them from moving outside the mined area.

There is a potential for natural attenuation in this system, since the conditions were originally reduced (low redox potential), especially if sulfate reducing conditions can be re-established. Undisturbed soil outside the mining area is also conducive to precipitation, complexation and immobilization of uranium due to the existing reducing conditions.

Many factors that were not measured in this paper need to be addressed in future studies. Additional measurements of redox potential and redox speciation of U, Fe, and Mn would help improve our understanding and prediction of the remediation efficacy at this site. The influence of hydrological, chemical and microbial changes on the constituent concentrations in the remediated mine unit has not been documented or measured. The residence time, flow rate relative to original replacement of water, needs to be accurately measured over a span of time. More wells and information across the mined area, and between the monitoring wells and the mined area, are needed for a better understanding of remediation efficacy at future sites.

## Acknowledgements

The authors have no economic interests associated with Cameco. This study was not funded, approved or authorized by Cameco. All opinions expressed are solely those of the authors. All data were obtained from public sources. Detailed map of mine unit A and Fig. 2 and 4 are copyright Cameco Resources (formally PRI). A-Wellfield Ground Water Quality Stabilization Report, Highland Uranium Project. Submitted to Wyoming Department of Environmental Quality, permit to Mine no. 603-A2. Published with permission of Cameco Resources, granted 18JAN2012, by John Schmuck, Senior Permitting Manager.

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